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### (54) Preparation of fine particulate silica

(57) Organohalosilane or disilane is subject to pyro-  
genic hydrolysis in a diffusion flame of hydrogen and air,

thereby producing fine particulate silica having a large  
specific surface area useful as fumed silica.

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**Description**

This invention relates to an industrially advantageous process for preparing fine particulate silica, known as fumed silica having a large specific surface area.

Among conventional processes for the synthesis of fumed silica the most commonly used one is a pyrogenic hydrolysis process of burning a premix of silicon tetrachloride, hydrogen, and air as disclosed in Japanese Patent Publication (JP-B) No. 46274/1972. In the premix burning process, however, silica can deposit and grow on the burner nozzle to eventually clog the nozzle or cause the risk of backfire or blow-off. The process becomes more dangerous as the burner diameter increases, that is, the production scale increases.

It is proposed in JP-B 4652/1968 and 2013B/1971 to produce fumed silica by diffusion combustion of silicon tetrachloride. The process of diffusion burning silicon tetrachloride can solve the problems of the premix combustion, but imposes the burden on silicone manufacturers that the starting silicon tetrachloride must be newly synthesized from metallic silicon and hydrogen chloride.

It is also known from JP-B 38526/1981 and 54085/1983 to synthesize fumed silica by burning a premix of an organohalosilane and air. Since the organohalosilane itself is combustible, the flame has a higher temperature and an increased length, resulting in fumed silica having a smaller specific surface area. In fact, fumed silica products obtained in Examples of JP-B 38526/1981 have a specific surface area of 207 m<sup>2</sup>/g at maximum. In the premix combustion process, the flame temperature might be reduced simply by increasing the proportion of air. However increasing the proportion of air can cause blow-off in the premix combustion process, failing to provide continuous combustion.

The aim herein is to provide a new and useful process for making fine particulate silica, preferably having a large specific surface area while reducing or eliminating the above-mentioned operational problems.

We have found that when an organohalosilane or organohalodisilane is subject to pyrogenic hydrolysis in a diffusion flame of a combustible gas capable of burning to release water vapor and a free oxygen-containing gas, fumed silica can be synthesized in a simple manner without the risk of backfire or blow-off and without causing silica to deposit on the burner nozzle. We obtained fumed silica with specific surface area as large as 100 to 400 m<sup>2</sup>/g (as measured by a BET method). The starting material may be an organohalosilane or disilane which is available as a by-product from the synthesis of dimethyldichlorosilane from metallic silicon and an organohalide, for example. The process allows for use of readily available starting materials and reduces operational risks. The process is thus advantageous from both the industrial and economical aspects.

**BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1 is a cross-sectional view of one exemplary burner used in the practice of the inventive process.

5 FIG. 2 is a cross-sectional view of another exemplary burner used in the practice of the inventive process.

According to the present invention, fine particulate silica is prepared by effecting diffusion combustion of an organohalosilane or organohalodisilane with a combustible gas and a free oxygen-containing gas to form a diffusion flame for subjecting the organohalosilane or disilane to pyrogenic hydrolysis therein.

The starting material is any of organohalosilanes and disilanes. Those organohalosilanes or disilanes

15 having a boiling point of up to 200°C are preferred because they must be gasified for supply to the burner. Exemplary organohalosilanes include methyltrichlorosilane, methyldichlorosilane, trimethylchlorosilane, and dimethyldichlorosilane, and exemplary organohalodisilanes include 1,2-dimethyltetrachlorodisilane, 1,1,2-trimethyltrichlorodisilane, 1,1,2,2-tetramethyltrichlorodisilane, 1,1,1,2-tetramethyltrichlorodisilane. Preferred are organohalosilanes and disilanes which are available or obtained as by-products from the synthesis of dimethyltrichlorosilane from metallic silicon and an organohalide, with the methyltrichlorosilane being especially preferred. "Organo" is usually alkyl, preferably methyl.

20 The combustible gas capable of burning to release water vapor (H<sub>2</sub>O) is typically hydrogen gas while methane, propane and gaseous methanol are acceptable. The combustible gas is essential for effecting hydrolysis of silane and providing active OH groups to the silica surface. It also serves as a source for allowing a stable flame to continue.

25 35 The free oxygen-containing gas is preferably air for economy's sake.

Any desired e.g. conventional well-known diffusion combustion methods may be used for subjecting the halosilane or halodisilane to pyrogenic hydrolysis in a diffusion flame. Any of well-known burners may be used for burning the reactants. For example, simple triple or quadruple tube burners may be used. Any burner with diffusion combustion capability is useful.

40 Referring to FIG. 1, there is schematically illustrated a quadruple tube burner including a center tube 1 for feeding the organohalosilane or disilane. An air feed tube 2, a hydrogen feed tube 3, and an air feed tube 4 concentrically surround the center tube 1 from the inside to the outside. FIG. 2 shows another burner arrangement 45 50 wherein a triple tube assembly 5 includes a center tube 1 for feeding the organohalosilane or disilane, an air feed tube 2 and a hydrogen feed tube 3. A plurality of, four in the illustrated embodiment, triple tube assemblies 5 are distributed in a large tube 6 for feeding air. These burner arrangements are shown for exemplary purposes, and the invention is not limited thereto.

55 In one preferred embodiment, the organohalosilane or disilane is fed to the center tube 1 at a flow rate of

about 0.1 to 10 kg/h, especially about 1 to 5 kg/h, air is fed to the air feed tube 2 at a flow rate of about 0.02 to 10 Nm<sup>3</sup>/h, especially about 0.2 to 5 Nm<sup>3</sup>/h, hydrogen is fed to the hydrogen feed tube 3 at a flow rate of about 0.02 to 10 Nm<sup>3</sup>/h, especially about 0.2 to 5 Nm<sup>3</sup>/h, and air is further fed to the outer tube 4 or 6 at a flow rate of about 0.02 to 10 Nm<sup>3</sup>/h, especially about 0.2 to 5 Nm<sup>3</sup>/h.

According to the present invention, fine particulate silica having a specific surface area as large as 100 to 400 m<sup>2</sup>/g, especially 200 to 400 m<sup>2</sup>/g as measured by a BET method can be produced in a simple manner without operational inconvenience. This surface area range is useful as fumed silica. The process of the invention thus has industrial advantages.

#### EXAMPLE

Examples of the present invention are given below by way of illustration and not by way of limitation.

#### Example 1

A quadruple tube burner as shown in FIG. 1 was used. Pyrogenic hydrolysis was carried out according to a diffusion combustion method by feeding 2.6 kg/h of methyltrichlorosilane through the center tube 1, 0.83 Nm<sup>3</sup>/h of dry air through the air feed tube 2, 0.39 Nm<sup>3</sup>/h of hydrogen gas through the hydrogen feed tube 3, and 0.83 Nm<sup>3</sup>/h of dry air through the outer air feed tube 4. The combustion gases were discharged at a flow rate of 40 Nm<sup>3</sup>/h for taking out the synthesized fumed silica. Note that the methyltrichlorosilane feed was heated with steam under a gage pressure of 2 kg/cm<sup>2</sup>G to form a gas feed to the burner.

Fumed silica was produced at a rate of 1.0 kg/h. It had a BET specific surface area of 215 m<sup>2</sup>/g.

#### Example 2

Fumed silica was synthesized by the same procedure as in Example 1 except that 2.6 kg/h of methyltrichlorosilane was fed through the center tube 1, 2.8 Nm<sup>3</sup>/h of dry air fed through the air feed tube 2, 0.83 Nm<sup>3</sup>/h of hydrogen gas fed through the hydrogen feed tube 3, and 0.83 Nm<sup>3</sup>/h of dry air fed through the outer air feed tube 4.

Fumed silica was produced at a rate of 1.0 kg/h. It had a BET specific surface area of 385 m<sup>2</sup>/g.

#### Example 3

Fumed silica was synthesized by the same procedure as in Example 1 except that 2.6 kg/h of methyltrichlorosilane was fed through the center tube 1, 0.57 Nm<sup>3</sup>/h of dry air fed through the air feed tube 2, 0.83 Nm<sup>3</sup>/h of hydrogen gas fed through the hydrogen feed tube 3, and 0.83 Nm<sup>3</sup>/h of dry air fed through the outer air feed tube 4.

Fumed silica was produced at a rate of 1.0 kg/h. It had a BET specific surface area of 121 m<sup>2</sup>/g.

#### Example 4

5 A quadruple tube burner as shown in FIG. 1 was used. Pyrogenic hydrolysis was carried out according to a diffusion combustion method by feeding 2.6 kg/h of a disilane mixture through the center tube 1, 2.8 Nm<sup>3</sup>/h of dry air through the air feed tube 2, 0.83 Nm<sup>3</sup>/h of hydrogen gas through the hydrogen feed tube 3, and 0.83 Nm<sup>3</sup>/h of dry air through the outer air feed tube 4. The disilane mixture used herein was obtained by synthesizing silanes from metallic silicon and methyl chloride by 10 a direct process to form a crude product and removing main products, organohalosilanes (typically dimethyl-dichlorosilane) from the crude product, leaving the disilane mixture containing 1,2-dimethyltetrachlorodisilane and other by-products. The disilane mixture was heated 15 with a heating medium at 250°C to form a gas feed to the burner.

Fumed silica was produced at a rate of 1.6 kg/h. It had a BET specific surface area of 250 m<sup>2</sup>/g.

#### Example 5

25 A funnel type burner as shown in FIG. 2 was used. Pyrogenic hydrolysis was carried out according to a diffusion combustion method by feeding 10 kg/h of methyltrichlorosilane through the center tubes 1, 3.3 Nm<sup>3</sup>/h of dry air through the air feed tubes 2, 1.6 Nm<sup>3</sup>/h of hydrogen gas through the hydrogen feed tubes 3, and 3.3 Nm<sup>3</sup>/h of dry air through the circumscribing tube 6. The combustion gases were discharged at a flow rate of 40 Nm<sup>3</sup>/h for taking out the synthesized fumed silica. Note that the methyltrichlorosilane feed was heated with steam under a gage pressure of 2 kg/cm<sup>2</sup>G to form a gas feed to the burner. No interference occurred between the flames.

30 40 Fumed silica was produced at a rate of 3.8 kg/h. It had a BET specific surface area of 180 m<sup>2</sup>/g.

#### Comparative Example 1

45 Pyrogenic hydrolysis was carried out by feeding a premix of 0.52 kg/h of methyltrichlorosilane, 0.81 Nm<sup>3</sup>/h of dry air, and 0.29 Nm<sup>3</sup>/h of hydrogen gas through a single tube having a diameter of 1/4 inch. The combustion gases were discharged at a flow rate of 40 Nm<sup>3</sup>/h as in Example 1.

50 Due to the high flame temperature, the fumed silica had a BET specific surface area of 61 m<sup>2</sup>/g.

#### Comparative Example 2

55 The same procedure as in Comparative Example 1 was carried out except that a premix of 0.62 kg/h of methyltrichlorosilane, 0.89 Nm<sup>3</sup>/h of dry air, and 0.20 Nm<sup>3</sup>/h

of hydrogen was fed. That is, an attempt was made to reduce the flame temperature by reducing the proportion of hydrogen relative to methyltrichlorosilane and increasing the proportion of air. The flame was blown off and extinguished.

Although some preferred embodiments have been described, many modifications and variations may be made thereto in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

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### Claims

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1. A process for preparing fine particulate silica, comprising subjecting an organohalosilane or organohalodisilane to pyrogenic hydrolysis in a diffusion flame of
  - a combustible gas capable of burning to release water vapor, and
  - a free oxygen-containing gas.
2. A process of claim 1 wherein the organohalosilane or organohalodisilane is obtainable as a by-product from the synthesis of dimethylchlorosilane from metallic silicon and an organohalide.
3. A process of claim 1 or claim 2 wherein the organohalosilane is methyltrichlorosilane.
4. A process of any one of the preceding claims wherein the combustible gas is hydrogen.
5. A process of any one of the preceding claims wherein the free oxygen-containing gas is air.

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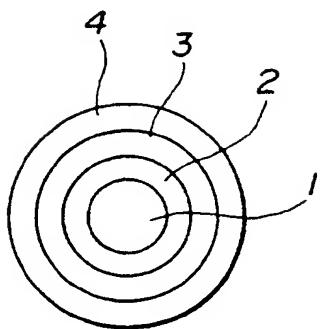
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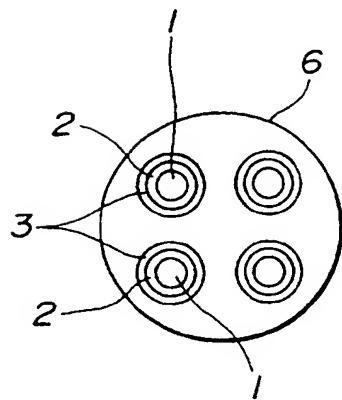
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**FIG.1**



**FIG.2**





## EUROPEAN SEARCH REPORT

Application Number  
EP 95 30 7145

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US-A-5 340 560 (ROHR ET AL) * claims 1-3 *	1,3	C01B33/18
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A	DE-A-35 25 802 (BAYER AG) * column 3, line 11 - line 27 *	1	
	---		
A	FR-A-2 451 343 (WACKER-CHEMIE GMBH) * page 3, line 9 - page 4, column 17; claim 1 *	1,3	
D	& JP-B-58 054 085 (...)		
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A	FR-A-2 351 052 (WACKER CHEMIE G.B.M.H.) * page 1, line 34 - page 3, line 13; claim 1 *	1	
D	& JP-B-56 038 526 (...)		
	---		
A	EP-A-0 097 378 (WACKER CHEMIE GMBH) * page 4, line 23 - page 5, line 12; claim 1 *	1	
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			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C01B
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
BERLIN	26 January 1996	Clement, J-P	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone	T : theory or principle underlying the invention		
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